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APPLICATION OF ULTRA VIOLET RADIATION IN OXIDATION POLYCYCLIC AROMATIC HYDROCARBON

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ABSTRACT

This oxidative process is one of the chief degradation pathways for PAHs in the natural aquatic environment. Photodegradation products of the following PAHs are characterized: naphthalene in vapor, phenanthrene in silica-air inter-phase anthracene in aqueous and organic solvents pyrene in soil surface or on carbon benzo[a]pyrene in aqueous media and some heterocyclic compounds in solutions or on solid surfaces. Since then, characterization of photoproducts of some PAH in aqueous or water/organic solvent mixtures are available: naphthalene pyrene benz[a]anthracene methyl substituted BAs, 1-hydroxypyrene, and 1-aminopyrene (AP).

KEYWORDS:

INTRODUCTION

oxidative process is one of the chief degradation pathways for PAHs in the natural aquatic environment. Photodegradation products of the following PAHs are characterized.

Photo chemical Reactions

1.formylcinnamaldehyde (II), and 2-carboxycinnamaldehyde (III) compound I be formed via the 1,4-naphthoquinone intermediate, and compounds II and III be from the breaking of the C1-C2 bond in naphthalene.

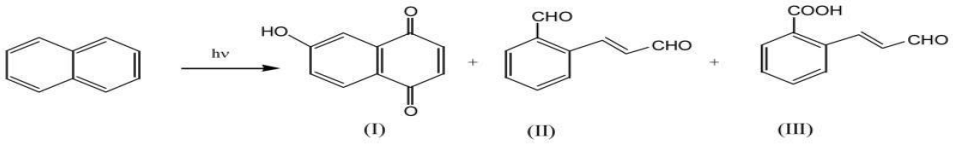

Fig. 1: Photochemical reaction of naphthalene in aqueous solution.

2. The photochemical reaction of anthracene and benz[a]anthracene (BA) follows the same pattern because they both have two most reactive positions in the molecule: 9 and 10 positions in anthracene and 7 and 12 positions in BA. Molecular orbital calculations show that the 7 and 12 positions in BA and methyl substituted BAs have the highest electron density Upon light irradiation, both anthracene and BA react with oxygen to form endoperoxides. Rearrangement and further oxidation of the endoperoxides lead to the formation of quinones.

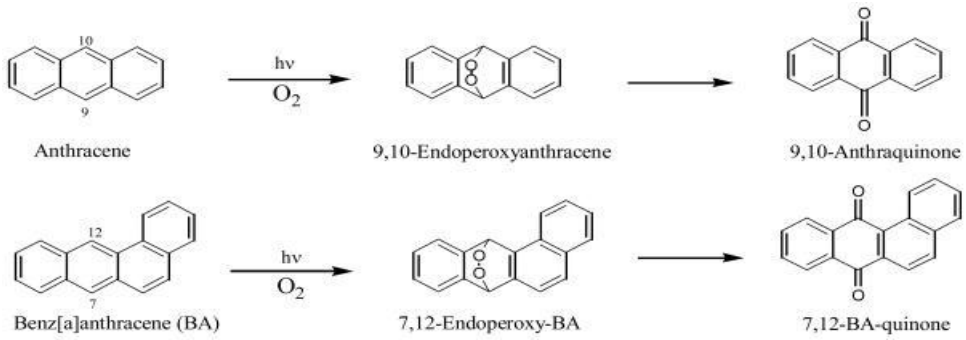

Figure-2: Photo-oxidation of anthrancene and benz[a]anthracene in aqueous solution.

3. Irradiation of 7,12-dimethyl-BA in aqueous solutions leads to the formation of 7,12-endoperoxide and subsequently to 7,12-BA-quinone. In addition, the methyl groups can also be oxidized during the photolysis, yielding first hydroxymethyl followed by further oxidation to formyl groups.

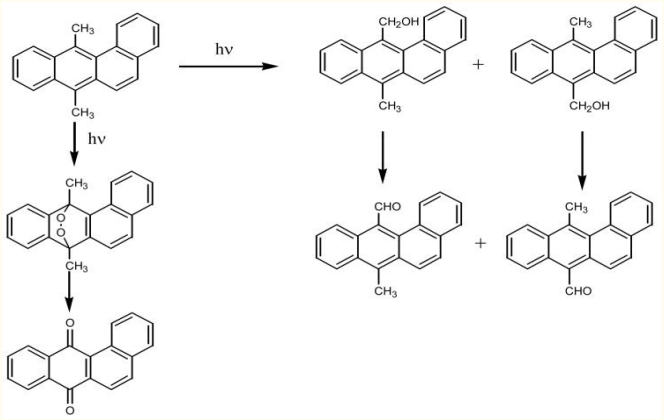

Figure-3: Photo-oxidation of 7,12-dimethylbenz[a]anthracene in aqueous solution.

4.Photolysis of pyrene yields 1,6- and 1,8-pyrenequinones as stable products whether in aqueous solution or in surfactant media If pyrene is irradiated by light on soil, eight photoproducts are detected with five of them identified structurally. They include the two pyrenequinones detected in the aqueous solution photolysis, two pyrenediols, 1,6- and 1,8-pyrenediol, and a pyrene dimer, 1,1′-bipyrene are also identified. More than 20 photoproducts are detected if pyrene is irradiated by sunlight on filter paper. The authors separated the oxygenated and the acidic fractions of the photoproducts and found that both fractions are more mutagenic toward *Salmonella typhimurium* bacteria with or without S-9 activation. The same test with the pure 1,6- or 1,8-pyrenequinone indicates that the mutagenicity of the mixture is not from the quinoes, but from other unknown oxygenated photoproducts.

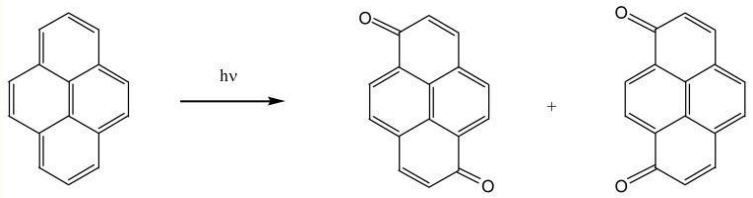

Figure 4: Photo-oxidation of pyrene in solution.

5.The most widely studied PAH is benzo[a]pyrene (B[a]P). Photolysis of B[a]P in aqueous solution yields 1,6-, 3,6-, and 6,12-B[a]P-quinones and in benzene yields a ring open product (I) in addition to those three quinones). 6-Oxy-B[a]P radical is observed if B[a]P is irradiated. It is suggested that further oxidation of the 6-oxy-B[a]P yields the quinones. It is proposed that the oxy-radical of B[a]P is responsible for DNA damage caused by the combination of UV light and B[a]P.

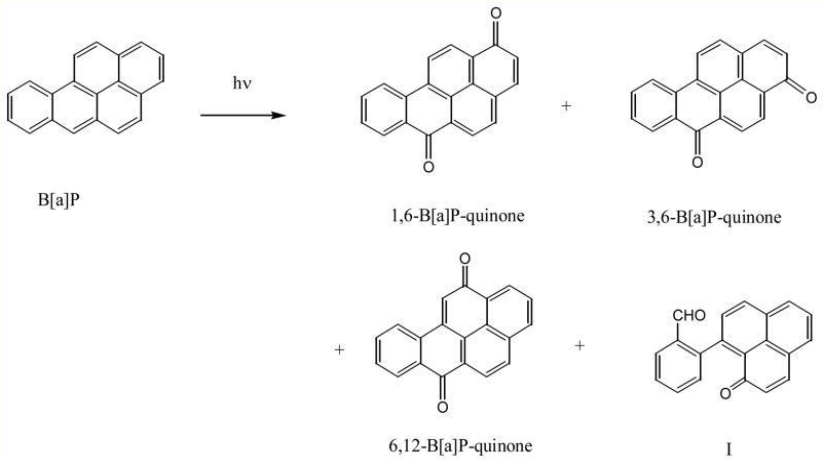

Figure 5: Photo-oxidation of benzo[a]pyrene in aqueous solution or benzene.

6.Hydroxy-PAHs are the oxidative metabolites commonly detected in the urine of animals or humans exposed to PAHs and are often used as biomarkers Among them, 1-hydroxypyrene (HP) is the most widely used biomarker for PAH exposure. Upon light irradiation in aqueous solutions, HP is converted to three pyrenequinones: 1,6-pyrenquinone, 1,8-pyrenequinones, and an unidentified quinone (). The 1,6 and 1,8-pyrenequinones are also among the photolysis products for pyrene in aqueous solutions The unidentified photoproduct has the correct molecular weight for a quinone, but the positions of the oxygen atoms are not determined.

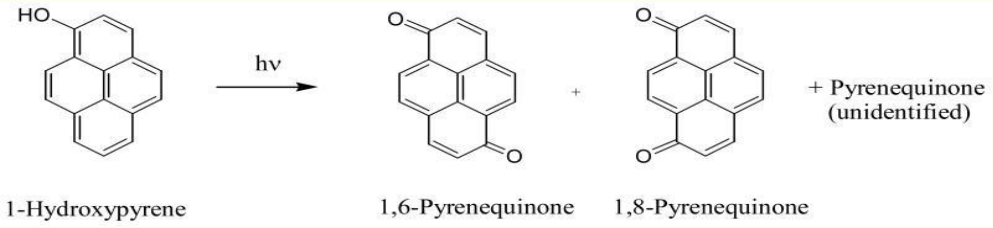

Figure 6: 7.Photo-oxidation of 1-hydroxypyrene in aqueous solution.

The photodegradation and photochemistry of nitro- and amino-PAHs have also been studied. Nitro-PAHs are a class of carcinogens detected in the atmosphere and some nitro-PAHs are more carcinogenic than their parent PAHs. Amino-PAHs are usually the metabolite of nitro-PAHs. The photochemical degradation of nitro-PAHs mainly leads to photo-oxidation products. The photochemical reaction rate of nitro-PAHs depends on the position of the nitro-substitution. Nitro groups *peri* to two hydrogen atoms is forced to be in a perpendicular orientation to the aromatic ring due to steric hindrance while nitro groups *peri* only to one hydrogen atom stay in a parallel orientation to the aromatic ring s, nitro-PAHs can be divided into two categories: those with the perpendicular and others with the parallel nitro groups relative to the aromatic ring. Photochemically, the former nitro-PAHs react faster than the latter due to a light activated nitrite rearrangement. nitro-PAHs having perpendicular nitro groups are less mutagenic than nitro-PAHs having the nitro group parallel to the aromatic rings. This toxicity difference is attributed to their inability to be metabolized into reactive intermediates (*N*-hydroxyamino-PAH) that can form covalent DNA adducts.

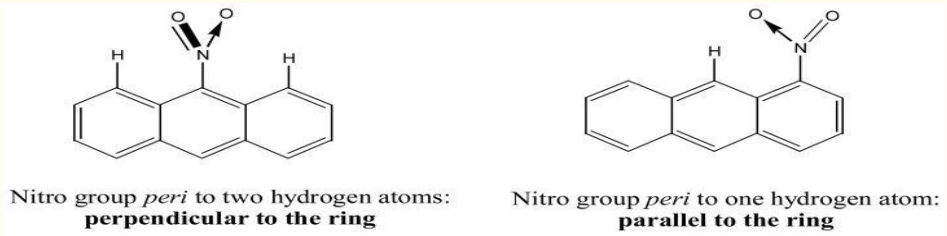

Figure 7: Nitro group orientation relative to the aromatic ring.

8. 9-Nitroanthracene is the first nitro-PAH whose photochemistry is studied. Photolysis of 9-nitroanthracene, whose nitro group is *peri* to two hydrogen atoms, yields mainly 9,10-anthraquinone. The authors proposed that the formation of the 9,10-anthraquinone is via the rearrangement of a nitrite intermediate. Upon absorbing light energy, the nitro group rearranges to become a nitrite. The nitrite in turn rearranges to place a nitroso group on the opposite side of the six-member ring bearing the nitrite. This position is one of the two most reactive sites in anthracene. Further oxidation leads to 9,10-anthraquinone. Some nitrites lead to dimer formation via free radical intermediates.

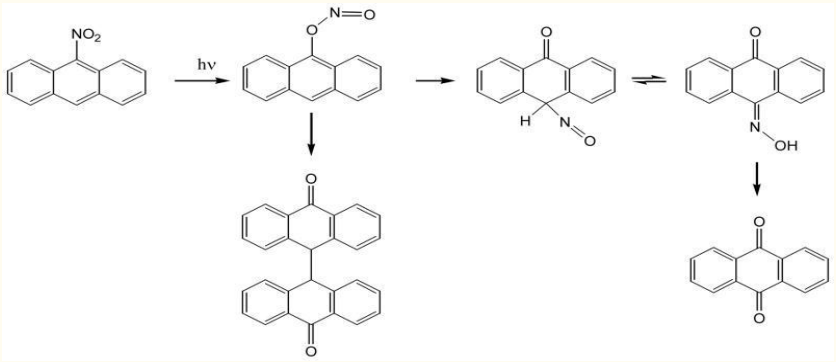

Figure 8: 9. Photo-transformation of 9-nitroanthracene.

Photolysis of 6-nitro-B[a]P, another nitro-PAH with the nitro group *peri* to two hydrogen atoms, yields 1,6-, 3,6-, and 6,12-B[a]P-quinones and 6-hydroxy-B[a]P, also via the nitrite intermediate. The three quinones are the same as the photolysis products of B[a]P.

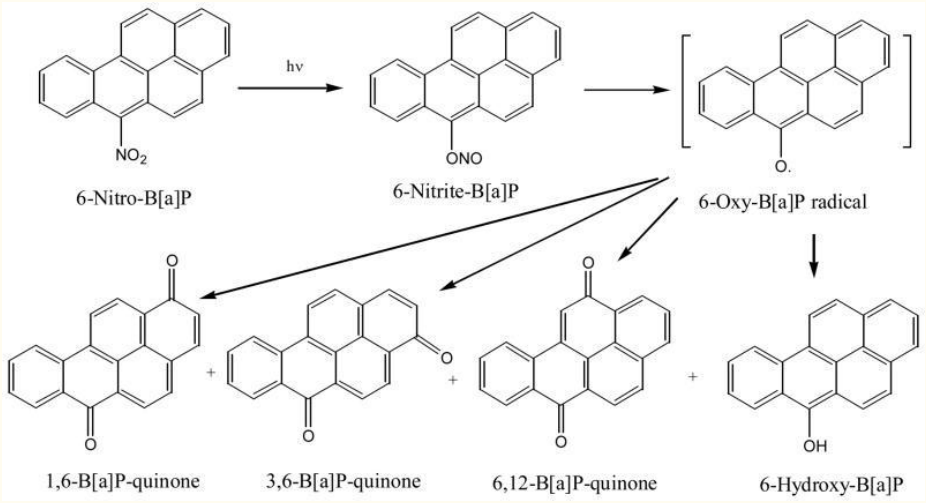

Figure 9: Photo-transformation of 6-nitrobenzo[a]pyrene.

10.Unlike 9-nitroanthracene, the rearrangement of the nitrite does not form the nitroso substituted compound because the nitroso group does not have a reactive carbon in 6-nitro-B[a]P as it does in 9-nitro-anthracene to bind to. Thus nitric oxide is released into the solution by the photolysis of 6-nitro-B[a]P. The authors claim that the nitric oxide released can cause DNA single strand cleavage. Also, photolysis of 1- or 3-nitro-B[a]P does not result in the same intermediates, although their photoproducts have not been characterized. In these two compounds, the nitro group is *peri* only to one hydrogen atom.

10.Irradiation of a 10% methanolic solution of 7-nitro-BA or 5-methyl-7-nitro-BA yields mainly the respective 7,12-BA-quinone. Irradiation of 12-methyl-7-nitro-BA does not produce the 7,12-BA-quinone. The main photoproduct isolated matches the molecular mass for 12-methyl-12-nitrosobenz[a]anthracen-7-one, the rearrangement intermediate for a 9-nitroanthracene-type reaction discussed above. The difference is that the presence of the 12-methyl group prevented further oxidation to 7,12-BA-quinone.

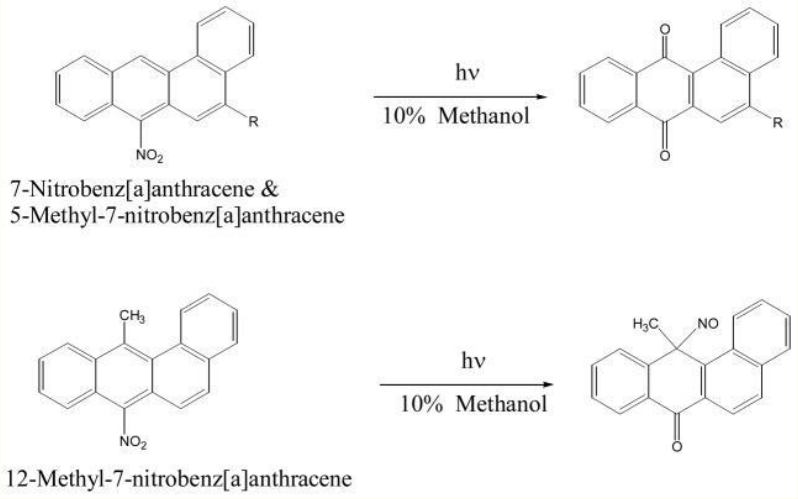

Figure 10: 11.Photo-transformation of 7-nitrobenz[a]anthracene and its methyl derivatives.

Unlike the nitro-PAHs that have the perpendicular nitro substituent, nitro-PAHs with a parallel nitro substituent are comparatively more stable under light irradiation. The photochemical reaction of these nitro-PAHs is complex due to the formation of complex mixture of photoproducts. This is probably why most of these photodegradation products have not been isolated and characterized, although the photodegradation of some of this type of nitro-PAHs have been studied To have a look of the difficulty of studying the photochemical reaction of this type of nitro-PAHs, one can look at the nine photodecomposition products for 1-nitropyrene). Several publications contributed to the identification of some of the nine photoproducts: pyrene quinone (no information

about the position of the oxygen) 1-hydroxypyrene, and several monohydroxy-1-nitropyrenes.

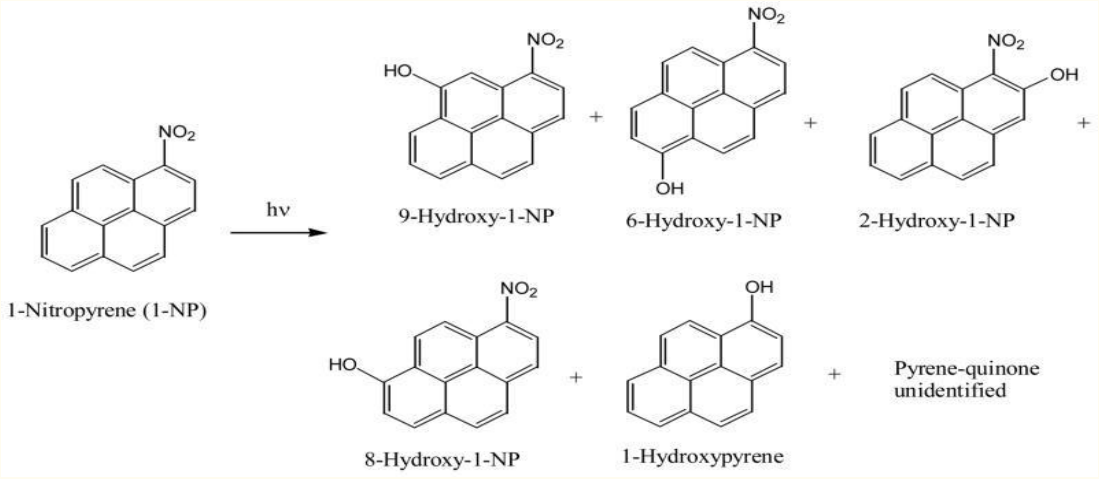

Figure 11: Photo-transformation of 1-nitropyrene.

12. The photodegradation of other nitro-PAHs that have been studied includes 2-nitroanthracene, 2- and 4-nitropyrene, 1,8-dinitropyrene, 3-nitrofluoranthene, 1- and 3-nitro-B[a]P, 9-nitrodibenz[a,c]anthrancene, and 7-nitrodibenz [a,h] anthracene. But their photoproducts have not been identified.

It was found that photolysis of amino-PAHs generates direct acting mutagens. Photolysis of 2-aminofluorene converts it into 2-nitrosofluorene, 2-nitrofluorene, and 2-amino-9-fluorenone Both the nitro and nitrosofluorenes are direct acting mutagens.

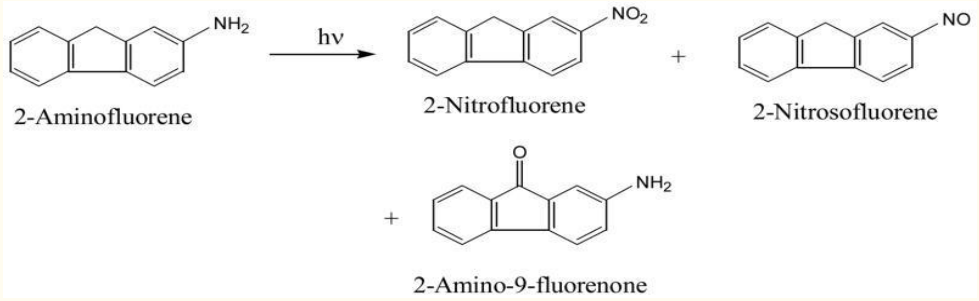

Figure 12: Photo-oxidation of 2-aminofluorene in aqueous solution.

13.Photolysis of 1-aminopyrene (AP) was first reported to produce the direct acting mutagen 1-nitropyrene and several other unidentified photoproducts. A more careful examination of the photochemical reaction products reveals that 1-nitrosopyrene, 1-hydroxyaminopyrene and some pyrene-quinone dimers are also formed in addition to 1-nitropyrene. Therefore, a progressive photo-oxidation mechanism is proposed. In this mechanism, the formation of 1-hydroxyaminopyrene is of particular interest because this is also the reactive intermediate that can form DNA covalent adducts from the enzymatic reduction of nitro-PAHs. Indeed, irradiation of AP together with calf thymus DNA, some AP-DNA covalent adducts are detected.

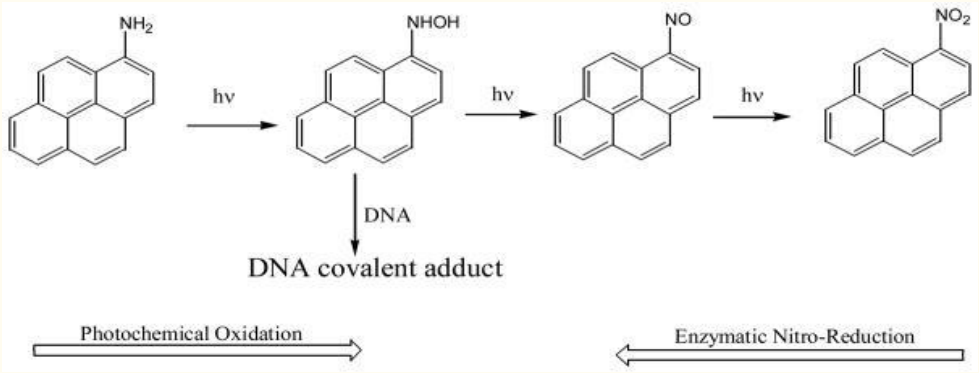

Figure 13: Photo-oxidation of 1-aminopyrene in aqueous solution.

Halogenated PAHs (chloro and bromo-PAHs) are also detected in the environment and are found to be carcinogenic. So far there has been neither phototoxicity study nor study of their photochemical reaction appeared in the literature.

CONCLUSION

In conclusion, the way the photochemical reaction of various PAHs proceeds depends on the structure of the PAHs themselves, the number of fused rings, the arrangement of the rings, the substituent type and position, as well as the coexisting molecules and solvents.

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